Surface Complexation Theory: Multispecies Ion Exchange Equilibria

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Introduction

Inorganic and organic ion exchangers consist of either a crystalline or a polymeric matrix and functional groups. Depending on the pH value of the liquid phase, these groups can either be protonated or dissociated. By this means exchangers are able to interact with ions from the liquid phase. There is a large variety of such interactions: they may be due to electrostatic and van der Waals forces, heteropolar and covalent binding, or coordination forces. The resulting sorption phenomena take place at the inner pores and/or surface of the exchangers.

The surface charge generates an electric potential normal to the surface. Consideration of the resulting electrostatic interactions has led to several theoretical descriptions, e.g. the Helmholtz, Gouy–Chapman and Stern models. Modern theoretical approaches consider the adsorption of counterions as a result of chemical interactions between the surface groups and dissolved species. Sorption of protons or of any other kind of ion is treated as a local equilibrium reaction. Specific (for protons and hydroxyl ions) and non-specific interactions lead to the formation of ion pairs at the surface that are designated as surface complexes. Different kinds of surface complexes can be discriminated.

Spectroscopic investigations of surfaces have given rise to the assumption that more than one single layer has to be assumed to account for the uptake of counterions. A typical approach used by many authors is the triple-layer model consisting of surface, inner and outer layers.

A further refinement of the triple-layer model is the approach developed by Horst. In this model individual sorption layers are credited to each kind of counterions. The respective theoretical approach allows the description of pure cation or anion exchange equilibria as well as of amphoteric equilibria encountered with activated alumina or activated carbon.

Theory

Amphoteric Reactions at a Charged Surface

Derivation of the mathematical relationships uses a generalized exchanger whose surface contains S–OH groups as functional sites. In aqueous systems these surface groups can be protolysed in two different ways.

In acid media the surface may be protonated according to:

$$S\text{–}OH + H^+ \Leftrightarrow S\text{–}OH_2^+ \qquad [1]$$

In order to maintain the condition of electroneutrality the charge on the surface has to be balanced by the negative charge of an anion, e.g.:

$$S\text{–}OH_2^+ + Cl^- \Leftrightarrow S\text{–}OH_2Cl \qquad [2]$$

Therefore, in sufficiently acid media, a sorption of acids takes place similar to the uptake by weakly basic exchange resins.

In alkaline solutions the surface hydroxyl groups can dissociate and hand protons over to the liquid phase:

$$S\text{–}OH \Leftrightarrow S\text{–}O^- + H^+ \qquad [3]$$

The negative surface charge has to be balanced by cations, e.g. by sodium ions:

$$S\text{–}O^- + Na^+ \Leftrightarrow S\text{–}ONa \qquad [4]$$

Together the formal equation [3] and [4] represent a cation exchange on an arbitrary cation exchanger.

Each of the above models holds for the uptake of acids or the exchange of protons for other monovalent cations in arbitrary pure anion or cation exchange processes. If the state of equilibrium is considered for an amphoteric exchanger and a liquid phase containing different cations and anions, then the uptake of anions will decrease with increasing pH value until the sorption is completely suppressed. In the same direction the cation exchange of protons for cations increases. The pH regions of almost exclusive cation and anion sorption are separated by a maximum of noncharged surface groups. In this transition region sorption of both cations and anions occurs. At the point of zero charge, therefore, the surface is covered with equal amounts of equivalents of positively and negatively charged counterions.

Surface Model Assumptions

During the protonation, or dissociation, of the surface OH groups either a negative or a positive surface

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potential is generated, depending on the pH and on the ionic strength of the liquid phase. Therefore, the respective counterions are subject to an attraction while the co-ions are rejected. Due to the sorption of counterions at functional groups, the surface potential is partly decreased. Unlike the description widely used in the literature, it is assumed that each kind of counterion is located at a characteristic distance from the surface. Thus, ordered double or 'Stern' layers are formed. Ion pairs between surface groups and counterions in the ordered layer are designated as surface complexes. Excess charges at the surface are balanced by counterions in the diffuse layer, which also contains co-ions. As a consequence, the surface potential continuously decreases normal to the surface to zero in the liquid phase. The equilibrium between solid and liquid phases is mainly dominated by protolytic reactions. In this way, the protons are the potential-determining species.

For a system with Cl^- and Na^+ ions the schematic arrangement of counterions and co-ions and the corresponding development of the potential are plotted in **Figure 1**. With respect to the radii of the hydrated species, the anion layers are assumed to be closer to the surface than those of the cations. (Cl^- and Na^+ ions are used as model counterions. Individual properties are not taken into account. Furthermore, the absolute values of the potential in the different layers are of no importance for the further mathematical derivations.)

General Sorption Equilibrium Relationships for an Amphoteric Surface

The derivation of equilibrium relationships makes use of the following assumptions:

1. The functional groups are uniformly distributed across a plane surface.

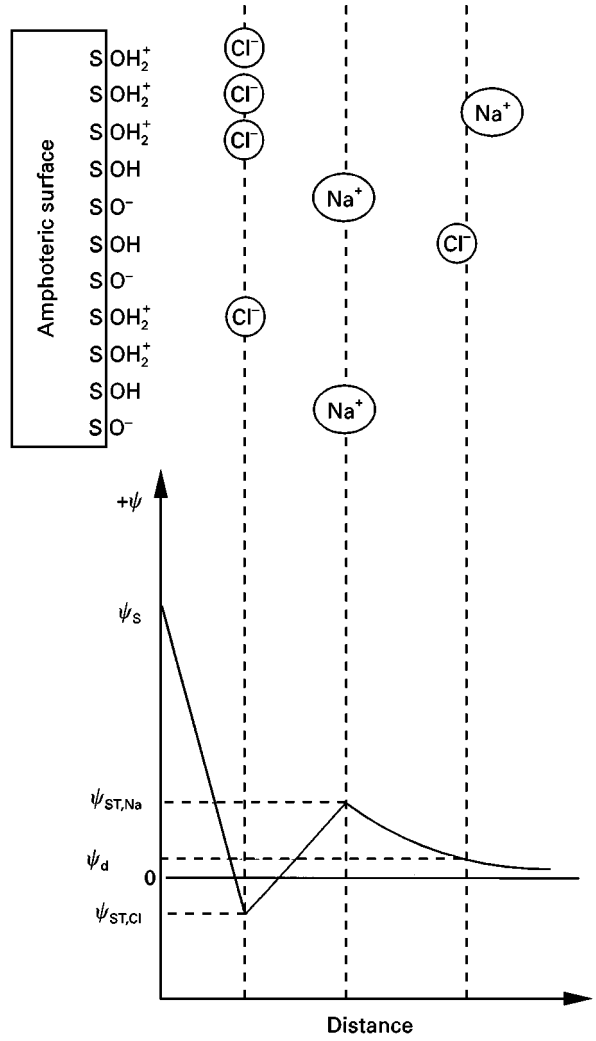

Figure 1 Schematic arrangement of ions at the amphoteric surface of activated alumina and the respective development of electrical potential.

2. Activity coefficients in the exchanger phase are assumed to be 1.
3. Any ion exchange develops as the replacement of one surface complex by a new one. As a consequence, an oxide valence is defined that is equal to the smallest common multiple of the valences of the counterions.

For the derivation of the equilibrium relationships a simple system with Cl^- and Na^+ ions is considered. The protolytic reactions at the surface are considered as local equilibria that can be described by the mass action law. The formation of the two surface complexes can be described by the respective formation constants, K (see **Table 1** for explanation of symbols used).

Protonation

$$S\text{–}OH + H_s^+ \Leftrightarrow S\text{–}OH_2^+ \qquad [5]$$

$$K_H^+ = \frac{c(S\text{–}OH_2^+)}{c(H^+)_s \cdot c(S\text{–}OH)} \qquad [6]$$

where c is the concentration of the species in parentheses in mol L^{-1}.

Dissociation/neutralization

$$S\text{–}O^- + H_s^+ \Leftrightarrow S\text{–}OH \qquad [7]$$

$$K_H^- = \frac{c(S\text{–}OH)}{c(S\text{–}O^-) \cdot c(H^+)_s} \qquad [8]$$

The sorption of counterions leading to two further surface complexes is considered in an analogous way.

Sorption of anions

$$S\text{–}OH_2^+ + Cl^- \Leftrightarrow S\text{–}OH_2Cl \qquad [9]$$

$$K_{Cl}^- = \frac{c(S\text{–}OH_2Cl)}{c(S\text{–}OH_2^+) \cdot c(Cl^-)_s} \qquad [10]$$

Sorption of cations

$$S\text{–}O^- + Na^+ \Leftrightarrow S\text{–}ONa \qquad [11]$$

$$K_{Na}^+ = \frac{c(S\text{–}ONa)}{c(S\text{–}O^-) \cdot c(Na^+)_s} \qquad [12]$$

Symbols with subscript 's' designate concentrations in the respective Stern layer. These unknown quantities can be expressed in terms of the concentrations in the liquid phase by means of the Poisson–Boltzmann relationship:

$$c(i)_x = c(i) \times \exp\left\{-\frac{z(i)F}{RT} \times \psi_x\right\} \qquad [13]$$

Here $c(i)_x$ represents the concentration of species i at position x in an electric field, $z(i)$ is the valence of species i, F is the Faraday constant, ψ_x is the electrical potential at position x, R is the gas constant, and T is the temperature in Kelvin.

The uptake of anions develops as the simultaneous sorption of protons and chloride ions. Since we have a sequence of reactions, the equilibrium of this common sorption can be expressed by the product of the respective formation constants:

$$K_{Cl}^H = K_H^+ \times K_{Cl}^- \qquad [14]$$

Table 1

Symbol	*Unit*	*Definition*
A_0	$m^2\ g^{-1}$	Specific surface area
$c(i)$	mol L^{-1}	Concentration of species i
$c(i)_s$	mol L^{-1}	Concentration of species i in the Stern layer
$c(i)_x$	mol L^{-1}	Concentration of species i at position x in an electrical field
$C(i, j)$	F m^{-2}	Electric capacitance of capacitor formed by the layers of species i and j
$C(S, i)$	F m^{-2}	Electric capacitance of capacitor formed by the surface and the layer of species i
F	A s	Faraday constant
K_j^i		Equilibrium constant of surface reaction
L	L	Volume of liquid phase
LS	—	left-hand side expression of eqns [38] and [39]
$m(H, j)$	—	Abbreviation, defined by eqn [22]
$q(i)$	mol g^{-1}	Oxide loading with species i
q_{max}	mol g^{-1}	Maximum exchanger loading
Q_j^i	—	Generalized separation factor
R	J mol^{-1} K^{-1}	Gas constant
S	g	Mass of sorbent
S–		Abbreviation used to designate the surface
T	K	Temperature
V	—	Sign of charge
$y(i)$	—	Dimensionless loading with species i
$y(i, i)$	—	Probability of the presence of two adjacent ions, i at the surface
$z(i)$	—	Valence of species i
σ_i	A s m^{-2}	Surface charge density of layer with ions i
ψ_x	V	Electrical potential at position x

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The uptake of cations, however, develops as the competitive sorption of protons and sodium ions. As a consequence, the equilibrium of the cation exchange is expressed by the ratio of the corresponding formation constants:

$$K^{H}_{Na} = \frac{K^{-}_{H}}{K^{+}_{Na}} \qquad [15]$$

By means of eqns [6]–[15] one obtains:

$$K^{H}_{Cl} = \frac{c(S\text{–}OH_2Cl)}{c(S\text{–}OH)\cdot c(Cl^-)\cdot c(H^+)} \times \exp\left\{+\frac{F}{RT}(\psi_S - \psi_{Cl})\right\} \qquad [16]$$

$$K^{H}_{Na} = \frac{c(S\text{–}OH)\cdot c(Na^+)}{c(S\text{–}ONa)\cdot c(H^+)} \times \exp\left\{\frac{F}{RT}(\psi_S - \psi_{Na})\right\} \qquad [17]$$

Multiplying by the volume of the liquid phase and dividing by the mass of sorbent, the concentrations of surface complexes are converted to exchanger loadings $q(OH)$, $q(Cl^-)$, and $q(Na^+)$ respectively; $(q(OH))$ denotes nonionized surface groups.

As a consequence, the first factor on the right-hand sides exclusively contains quantities that can be derived from experiments. Both expressions are designated as *generalized separation factors*, Q. After introducing dimensionless loadings with species i, $y(i) = q(i)/q_{max}$, where q_{max} is the maximum exchanger loading, the following expressions are obtained:

$$Q^{H}_{Cl} = \frac{q(Cl)}{q(OH)\cdot c(H^+)\cdot c(Cl^-)} = \frac{y(Cl)}{y(OH)\cdot c(H^+)\cdot c(Cl^-)} \qquad [18]$$

$$Q^{H}_{Na} = \frac{q(OH)\cdot c(Na^+)}{q(Na)\cdot c(H^+)} = \frac{y(OH)\cdot c(Na^+)}{y(Na)\cdot c(H^+)} \qquad [19]$$

Similar relationships can be derived for any monovalent counterion.

The difference of electrical potentials in the exponential terms of eqns [16] and [17] needs consideration about the surface charge densities in the series of electric capacitors formed by the surface, Stern and diffuse layers. As has been shown in earlier publications, the unknown differences in the electrical potential can be expressed in terms of the loading of the surface with Cl^- and Na^+ ions. After resolving the equations for the generalized separation factor one obtains:

$$\log Q^{H}_{Cl} = \log K^{H}_{Cl} + m(H, Cl) \times [-y(Cl) + y(Na)] \qquad [20]$$

$$\log Q^{H}_{Na} + m(H, Cl)\cdot y(Cl) = \log K^{H}_{Na} + m(H, Na)\cdot y(Na)] \qquad [21]$$

The terms $m(H, i)$ are given by the following equation:

$$m(H, i) = \frac{1}{12.303} \times \frac{q_{max}\cdot F^2}{A_0\cdot C(S, i)\cdot RT} \qquad [22]$$

where A_0 is the specific surface area and $C(S, i)$ denotes the capacitance of the capacitor formed by the surface and layer i. The derivation has been given in the literature.

For a system with an arbitrary number of monovalent counterions, the following relationship can be deduced from similar considerations:

$$\log Q^{H}_{i} = \log K^{H}_{i} + \sum_{j=2}^{i-1}\{m(H, j)\cdot V(j)\cdot y(j)\} + m(H, i)\sum_{i}^{n}\{V(i)\cdot y(i)\} \qquad [23]$$

$i = 2,3 \ldots, n$ index of counterions

$j = 2,3 \ldots, i-1$ running index

Hydrogen ions are always taken as component '1'. The factors $V(j)$ and $V(i)$ are the signs of the charge of the ions having the values of -1 for anions and $+1$ for cations. The first summation comprises counterions from index '2' to 'i − 1' (closer to the surface than species 'i'). The second summation considers the counterions with indices running from 'i' to 'n'. For a system with n counterions there are $n-1$ equations [23]. By subsequent evaluation of data all constants $\log K^{H}_{i}$ and $m(H, i)$ can be derived from the multicomponent system.

During the exchange of one divalent counterion for two monovalent ions, one divalent ion replaces two adjacent monovalent species at the surface, where at least one divalent species of counterion is present, the sorbent has to be assumed to have divalent functional sites in the mathematical treatment (assumption 3). As a consequence, a surface complex consisting of two sites and two monovalent counterions is defined that is replaced by a surface complex which consists of two sites with one divalent counterion. For a system with H^+, Na^+, Cl^- and SO_4^{2-} the generalized

separation factors are then given by the following expressions:

$$Q^{H}_{IISO_4} = \frac{c\{(S\text{–}OH_2)_2 = SO_4\}}{c\{S\text{–}OH,\ S\text{–}OH\} \cdot c(H^+)^2 \cdot c(SO_4^{2-})} \quad [24]$$

$$Q^{H}_{IICl} = \frac{c\{S\text{–}OH_2Cl,\ S\text{–}OH_2Cl\}}{c\{S\text{–}OH,\ S\text{–}OH\} \cdot c(H^+)^2 \cdot c(Cl)^2} \quad [25]$$

$$Q^{H}_{IINa} = \frac{c\{S\text{–}OH,\ S\text{–}OH\}}{c\{S\text{–}ONa,\ S\text{–}ONa\} \cdot c(H^+)^2} \quad [26]$$

Here the subscript II refers to calculation under the assumption of divalent functional sites.

The probability of two adjacent monovalent counterions i at the surface is given by:

$$y(i, i) = \left(\frac{y(i)}{\sum y(j)}\right)^2 \times \sum y(j) \quad [27]$$

where $\sum y(j)$ is the sum of dimensionless loadings of all monovalent counterions with valences $+1$ and -1.

By this means the above separation factors can be expressed as:

$$Q^{H}_{IISO_4} = \frac{y(SO_4) \cdot \{y(H) + y(Cl) + y(Na)\}}{y(OH)^2 \cdot c(H^+)^2 \cdot c(SO_4^{2-})} \quad [28]$$

$$Q^{H}_{IICl} = \frac{y(Cl)^2}{y(OH)^2 \cdot c(H^+)^2 \cdot c(Cl)^2} \equiv [Q^{H}_{ICl}]^2 \quad [29]$$

$$Q^{H}_{IINa} = \frac{y(OH)^2 \cdot c(Na^+)^2}{y(Na)^2 \cdot c(H^+)^2} \equiv [Q^{H}_{INa}]^2 \quad [30]$$

If divalent functional sites are assumed for systems with exclusively monovalent counterions, then the equilibrium parameters $\log K^{H}_{IIi}$ and $m_{II}(H, i)$ can be transformed to the parameters for monovalent functional sites according to:

$$\log K^{H}_{Ii} = \frac{\log K^{H}_{IIi}}{2} \quad [31]$$

$$m_{I}(H, i) = \frac{m_{II}(H, i)}{2} \quad [32]$$

The subscripts I and II refer to the assumption of either monovalent or divalent functional sites. If a system contains monovalent and divalent counterions the entire calculation has to assume divalent functional sites. Equilibrium parameters derived from systems with only monovalent counterions have to be converted corresponding to eqns [31] and [32].

Relationships for Pure Cation or Anion Exchange on Weak Electrolyte Resins

In the case of weakly acidic exchange resins there is no exchange of anions. Therefore, the terms for anions in the general equation [24] vanish. For a simple system with H^+ and Na^+ ions, eqn [21] simplifies to:

$$\log Q^{H}_{Na} = \log K^{H}_{Na} + m(H, Na) \cdot y(Na) \quad [33]$$

In a similar way, there is no exchange of cations by weakly basic exchangers. For the uptake of hydrochloric acid eqn [20] yields:

$$\log Q^{H}_{Cl} = \log K^{H}_{Cl} - m(H, Cl) \cdot y(Cl) \quad [34]$$

The uptake of anions by protonated functional groups is equivalent to the exchange of anions for hydroxyl groups:

$$S\text{–}OH \cdot H_2O + Cl^- \Leftrightarrow S\text{–}O_2Cl + OH^- \quad [35]$$

A similar theoretical development of the exchange of OH^- for Cl^- ions leads to the equilibrium relationship:

$$\log Q^{OH}_{Cl} = \log K^{OH}_{Cl} + m(OH, Cl) \cdot y(Cl) \quad [36]$$

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Relationships for Strong Electrolyte Exchangers

Relationships for the description of equilibria with strongly acidic and strongly basic resins can also be derived from the basic equation [23]. The difference, however, is that hydrogen ions cannot be assumed to be adsorbed in the innermost layer. In the case of the cation exchangers this can be explained by the fact that the exchanger is completely dissociated, even in the H^+ form. Furthermore, hydrated protons have a rather large diameter and, therefore, cannot be assumed to be located close to the surface. Similar considerations hold for strongly basic anion exchangers and hydroxyl ions. For both cases, therefore, the sequence of layers starts with the kind of counterions which in each is located the closest to the surface.

Liquid Phase Equilibrium Relationships

The liquid phase equilibrium is calculated by means of:

- the dissociation of water;
- the condition of electroneutrality; and
- mass balances for each component.

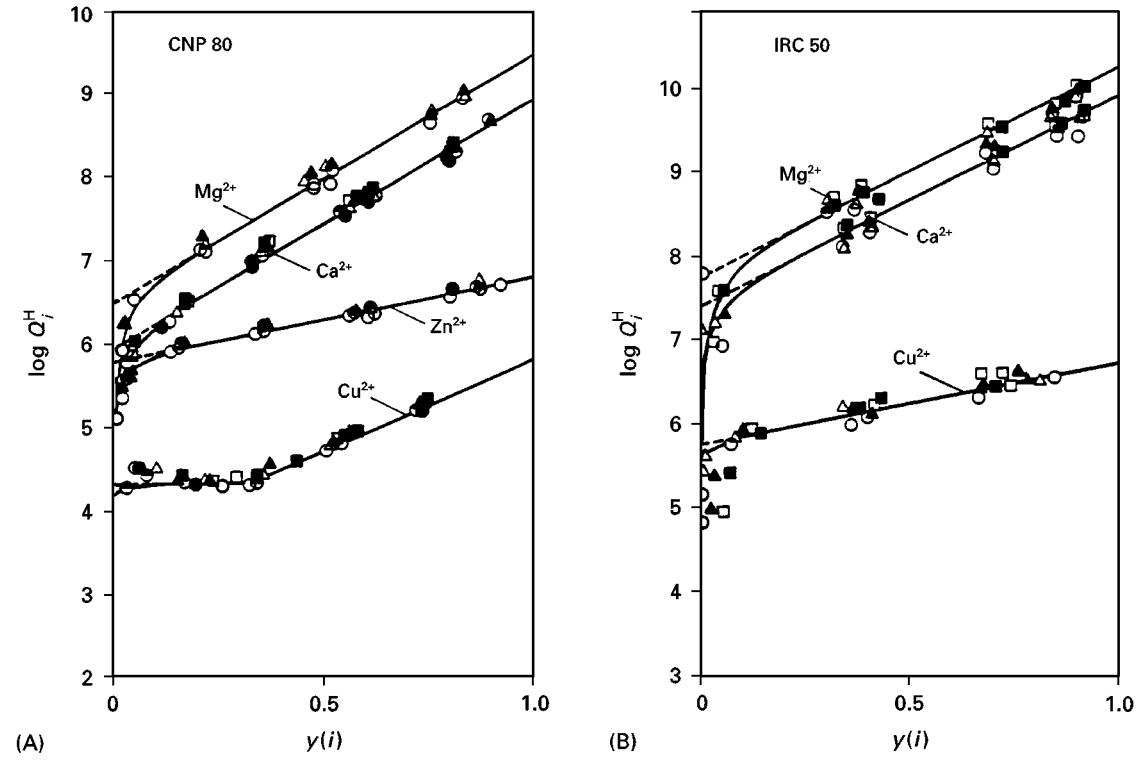

Figure 2 Development of the generalized separation factor for the weakly acidic ion exchange resins (A) LEWATIT CNP 80 and (B) AMBERLITE IRC 50 (by courtesy of Marcel Dekker Inc.).

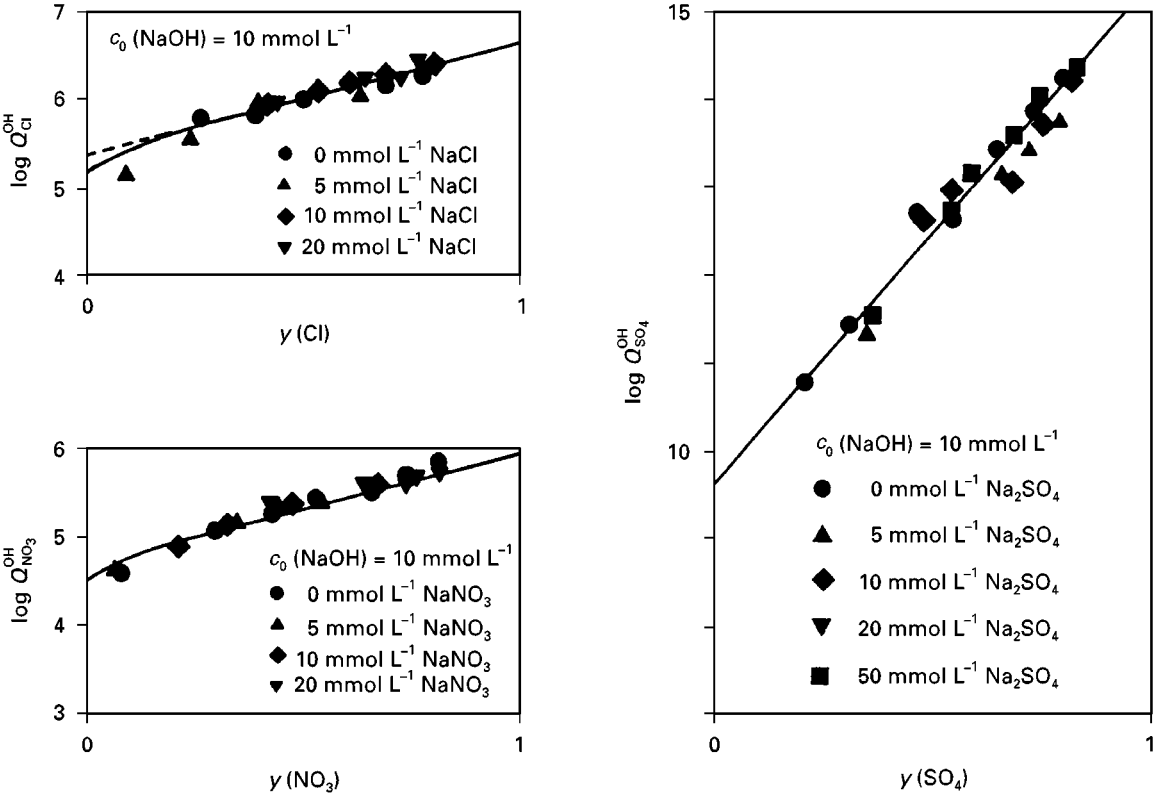

Figure 3 Development of the generalized separation factor for the weakly basic ion exchange resin AMBERLITE IRA 93 (by courtesy of Marcel Dekker Inc.).

Activity coefficients in the liquid phase can be calculated from the ionic strength using the extended Debye–Hückel relationship.

Experimental Evaluation of Equilibrium Data

General

Exchange equilibria have been determined for pure cation and anion exchangers as well as for amphoteric materials such as activated alumina and activated carbon. The pretreatment of these materials and the experimental conditions needed for obtaining proper equilibrium data have been described in detail in several publications. Cation concentrations can be measured by titration, photometric methods or by atomic absorption spectroscopy. Nitrate concentrations are measured photometrically, chloride and sulfate concentrations by ion chromatography.

In the case of pure anion or pure cation exchange, equilibria samples with increasing amounts of exchanger material are contacted with a fixed volume of the solution at constant temperature until equilibrium is obtained. Experiments with amphoteric equilibria are carried out at constant concentrations in the liquid phase and constant quantities of activated alumina or activated carbon in each of the samples. The volume/mass ratio is adjusted so that there is a substantial degree of sorption, as well as an equilibrium concentration that can be measured easily and with sufficient accuracy. Since the state of equilibrium is mainly dominated by the pH of the liquid phase, the pH value is varied in each series of samples. Details are described in the literature.

Evaluation of Data

For evaluation of equilibrium parameters the generalized separation factors have to be determined from equilibrium concentrations and resin loadings. These are then plotted against the respective dimensionless resin loading or the (algebraic) sum of resin loadings. In the case of binary systems with pure cation or anion exchange, the respective graphical representations directly yield the equilibrium parameters. The intersection of the linear relationship leads to $\log K$ and the slope of the straight line yields $m(i, j)$. **Figures 2–5** show examples for different types of exchangers.

The results show that linear relationships are obtained in most cases. Systematic deviations are found for small loadings. This is attributed to the neglect of counterions in the diffuse layer. As has been demonstrated by Horst for simple systems, when this layer is considered, excellent agreement is obtained. For strongly acidic exchangers this region is comparatively larger than for other resin types. Evaluation of data for the exchange of sulfate for chloride on strongly basic exchangers shows that there are two different straight lines. There are clearly two different layers that are subsequently 'filled'. Evaluation of data for a broad range of total concentrations up to 100 mmol L^{-1} in the liquid phase reveals identical development of the linear relationships. For the entire range of ionic strength investigated the parameters can, therefore, be considered as 'constant' equilibrium constants.

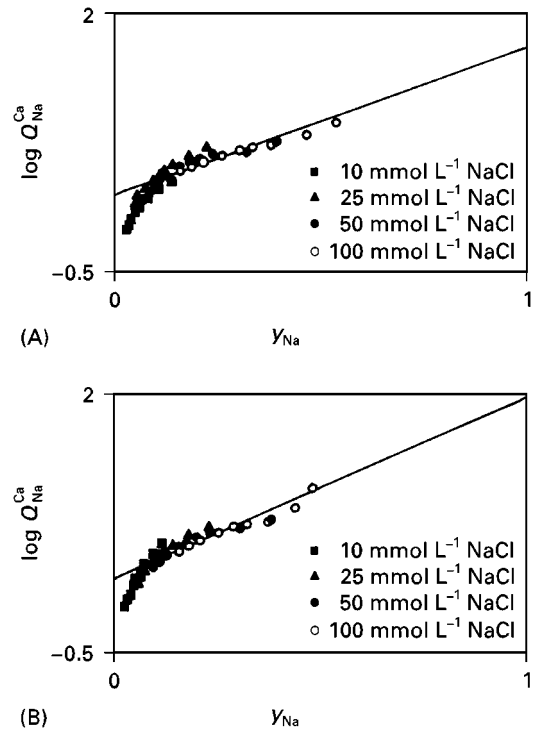

Figure 4 Development of the generalized separation factor for the exchange of calcium for sodium ions on two different strongly acidic resins. (A) Dowex HCRS; (B) LEWATIT S100.

Evaluation of amphoteric data requires a more sophisticated approach. The first step is the assumption of a certain sequence of layers. Evaluation of data starts with the evaluation of the equilibrium for the uptake of protons and ions in the first layer. The respective parameters are required for evaluation of the sorption of species in the next layer. Determination of the parameters for the third layer requires the sets of parameters for both the inner layers. This process has to be continued until all sets of binary parameters are derived. The sequence of a layers is assumed correctly if both the $\log K$ and $m(\mathrm{H}, i)$ values show a steady increase with increasing distance. If this conditions is not fulfilled the calculation must be repeated with a modified sequence. Considering a system of layers H^+, Cl^-, NO_3^-, Na^+ on activated alumina as an example, the equilibrium

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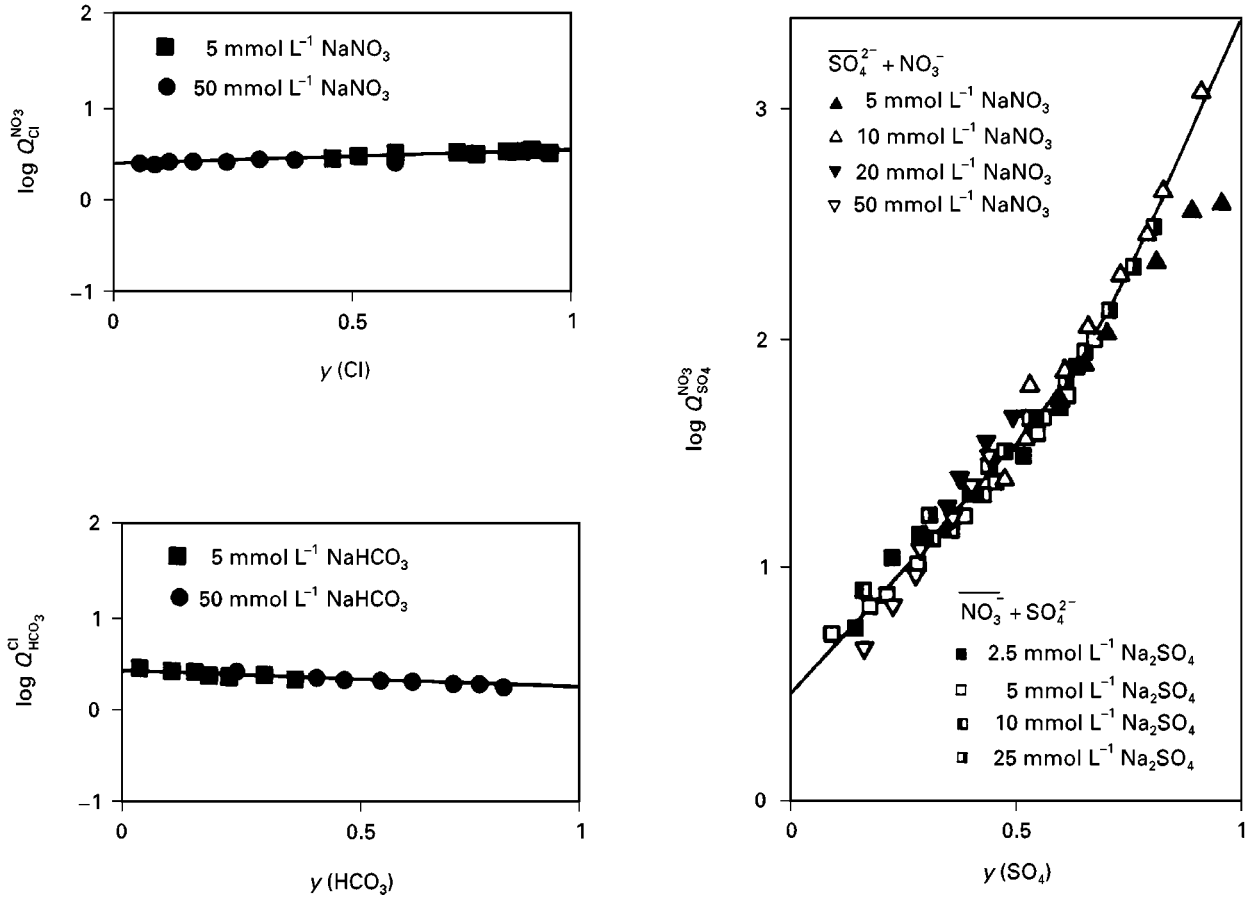

Figure 5 Development of the generalized spearation factor for the strongly basic ion exchange resin AMBERLITE IRA 410 (Reprinted from Höll, Horst, Franzreb and Eberle (1993) by courtesy of Marcel Dekker Inc.).

parameters can be evaluated from the following relationships:

$$\log Q_{Cl}^{H} = \log K_{Cl}^{H} + m(H, Cl) \cdot \{y(Na) - y(Cl) - y(NO_3)\} \quad [37]$$

$$\log Q_{NO_3}^{H} - m(H, Cl) \cdot \{-y(Cl)\} = \log K_{NO_3}^{H} + m(H, NO_3) \cdot \{y(Na) - y(NO_3)\} \quad [38]$$

$$\log Q_{Na}^{H} - m(H, Cl) \cdot \{-y(Cl)\} - m(H, NO_3) \cdot \{-y(NO_3)\} = \log K_{Na}^{H} + m(H, Na) \cdot y(Na) \quad [39]$$

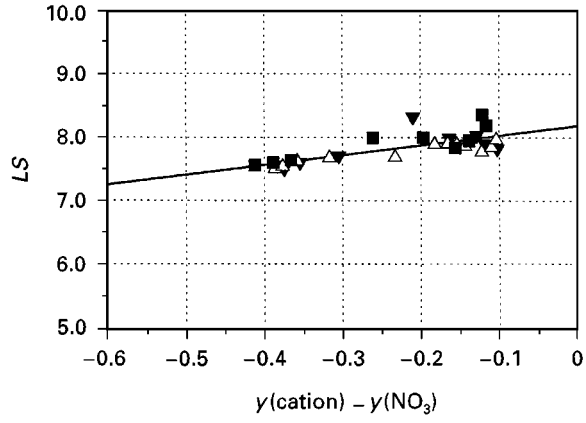

Figure 6 Development of the generalized separation factor for the uptake of nitrate by activated alumina (COMPALOX AN/V800) from a multicomponent system (cation = Na^+ or K^+). The symbols represent different experiments.

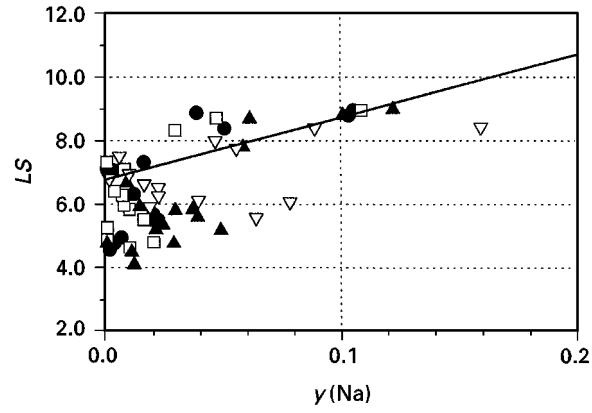

Figure 7 Development of the generalized separation factor for the sorption of sodium on COMPALOX AN/V800.

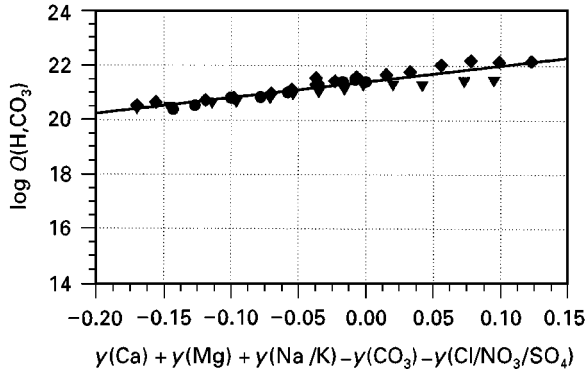

Figure 8 Development of the generalized separation factor for the sorption of carbonate species by activated carbon (NORIT ROW 0.8 Supra) from a multicomponent system.

Results of the evaluation of equilibrium data for the sorption of Cl^-, NO_3^- and Na^+ on activated alumina (COMPALOX AN/V800) are plotted in **Figures 6** and 7. Although the results for the uptake of sodium ions are not satisfactory, the data demonstrate that linear relationships are obtained.

Prediction of Multicomponent Equilibria

General

Prediction of arbitrary exchange equilibria requires a set of conditions to be fulfilled:

- conservation of mass
- electroneutrality on the liquid phase
- electroneutrality on the resin phase
- adjustment of equilibrium for the exchange of ions
- dissociation equilibria in the liquid phase.

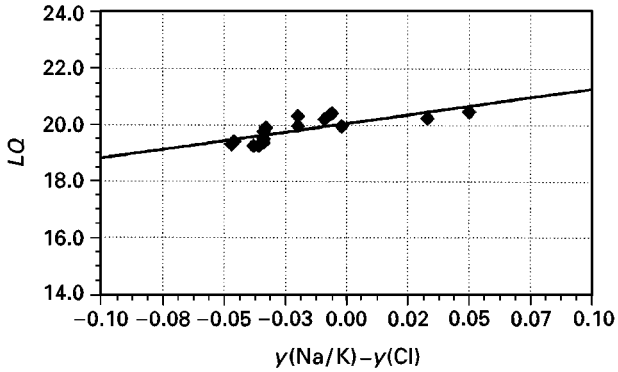

Figure 9 Development of the generalized separation factor for the sorption of chloride ions by activated carbon (NORIT ROW 0.8 Supra) from a multicomponent system. $LQ = \log Q(\mathrm{H, Cl}) + m_{II}(\mathrm{H, CO_3})y(\mathrm{CO_3}) - m_{II}(\mathrm{H, Ca})y(\mathrm{Ca}) - m_{II}(H, mg)y(\mathrm{mg})$.

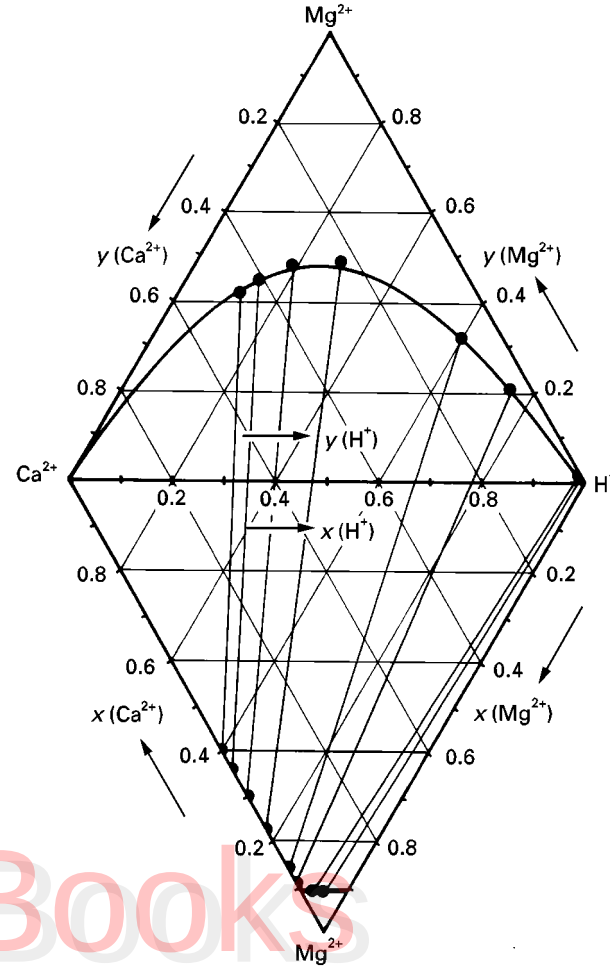

Figure 10 Comparison of experimental data and predicted equilibria for the ternary system $H^+/Mg^{2+}/Ca^{2+}$ on the weakly acidic resin LEWATIT OC 1046.

As can easily be shown, the number of equations is always greater than the number of unknown quantities. Therefore, some conditions are fulfilled automatically. The remaining set of coupled nonlinear equations must be solved by appropriate numerical methods.

Respective results for the uptake of inorganic ions by an activated carbon are plotted in **Figures** 8 and 9. With few exceptions, the equilibrium data satisfactorily fall on linear relationships as predicted by the theoretical approach.

Pure Cation or Anion Exchange

For prediction of multicomponent equilibria it is convenient if the binary parameters for the exchange of different counterions for the same reference ion have been deduced. For pure cation or anion exchange systems consideration of a three-component equilibrium with ions. A (reference ion), B and

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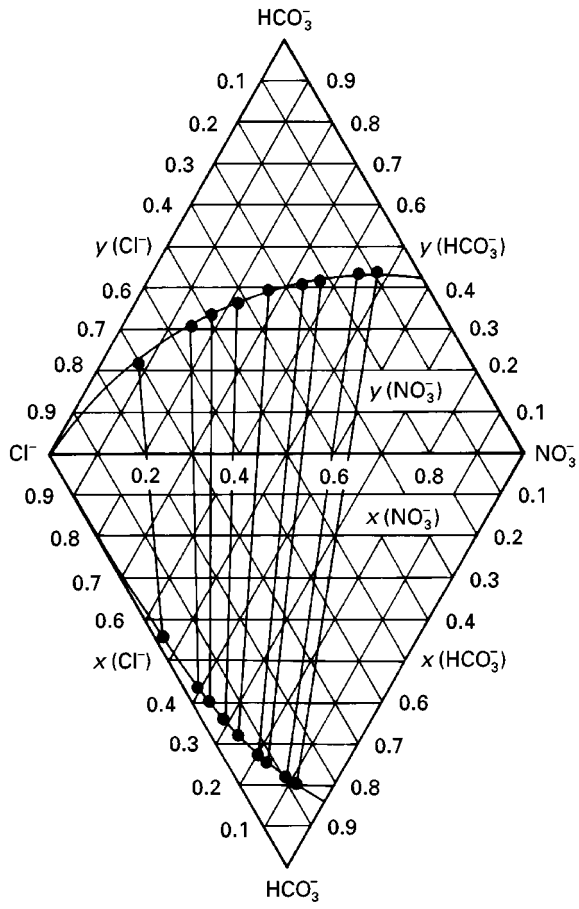

Figure 11 Comparison of experimental data and predicted equilibria for the ternary system $Cl^-/HCO_3^-/NO_3^-$ on the strongly basic resin AMBERLITE IRA 410.

C leads to the relationships:

$$\log Q_B^A = \log K_B^A + m(A, B) \cdot [y(B) + y(C)] \quad [40]$$

$$\log Q_C^B = \log K_C^B + m(B, C) \cdot y(C) \quad [41]$$

As has been demonstrated earlier, the binary parameters for the exchange of A versus B are the same as in the pure binary case. Also, the binary parameters for the exchange of A for C have been evaluated. In the above system, therefore, the parameters for the exchange of B for C are unknown. However, they can easily be calculated: the unknown parameter $\log K_C^B$ results from the definition:

$$\log K_C^B = \log K_C^A - \log K_B^A \quad [42]$$

For derivation of the unknown slope we make use of the fact that the sequence of layers can be considered as a series of layers of an electric capacitor. Since the definition of $m(i, j)$ contains the electric capacitance, C, we can make use of the well-known relationship for capacitances in series:

$$\frac{1}{C(A, C)} = \frac{1}{C(A, B)} + \frac{1}{C(B, C)} \quad [43]$$

Thus, one obtains:

$$m(B, C) = m(A, C) - m(A, B) \quad [44]$$

Similar relationships are obtained for systems with more than three counterions. Examples of a comparison between experimental results and equilibria predicted from binary data are given in **Figures 10–12.**

For amphoteric sorbents the individual equilibrium parameters are already determined during evaluation of data. Therefore, no additional calculations are required. **Figure 13** shows the comparison between experimentally determined oxide loadings and developments calculated by means of the set of equilibrium parameters determined previously. The data are plotted as relative loadings ($q(i)/q_{max}$) as a function of pH. The system contained the four components H^+, Cl^-, SO_4^{2-} and K^+. Obviously, sulfate ions are preferred over chloride species. The constant sulfate loadings for pH values below 5 are due to the constant initial sulfate concentration in the system. Only minor loadings with monovalent cations are observed. There is excellent agreement with the predicted loadings.

Figure 14 shows the results from one experiment with activated carbon and protons, carbonate, sulphate, calcium, magnesium and potassium as counterions. The relative loadings with both carbonate and nitrate ions decrease with increasing pH of the solution, while the loadings of calcium and potassium slightly increase. Nevertheless their uptake

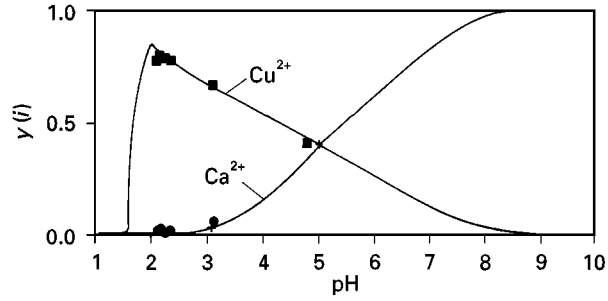

Figure 12 Comparison of experimental data and predicted equilibria for the ternary system $H^+/Ca^{2+}/Cu^{2+}$ on the chelating resin LEWATIT TP 207. C_0 (HCl) = 10 mmol L^{-1}; C_0 ($CuCl_2$) = 10 mmol L^{-1}. (From Horst and Höll (1997), copyright Academic Press.)

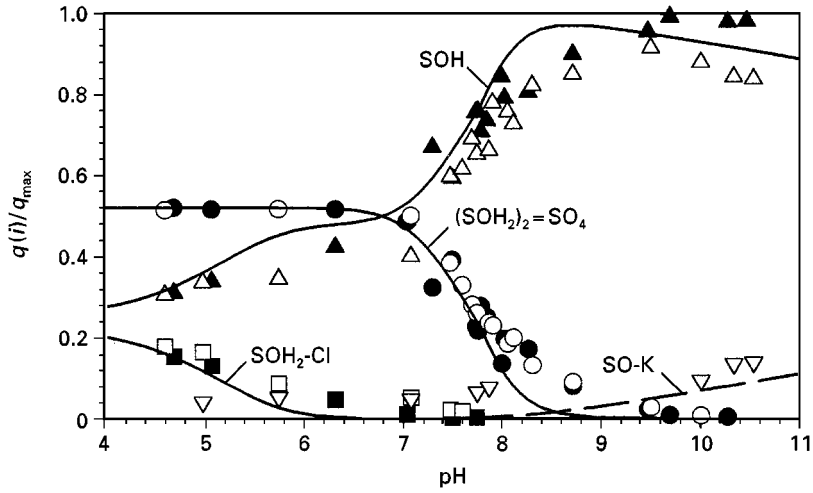

Figure 13 Comparison of experimental data and predicted loadings of activated alumina for a multicomponent system. Activated alumina: COMPALOX AN/V800.

remains small, indicating that there is only a small capacity for the uptake of cations. Again, there is good agreement with the predicted developments.

Applications

The principal advantage of the surface complexation theory lies in the fact that it can be applied to any normal or reaction-coupled ion exchange process for which other theoretical descriptions of equilibria fail.

One field of application is the prediction of multispecies exchange kinetics. This has been demonstrated by Franzreb, who included the description into the solution of the Nernst–Planck equations for several ternary and quaternary cases. The development of systems with strong and weak exchange resins and with normal and reaction-coupled multispecies processes could be predicted with excellent accuracy.

The surface complexation theory can also be easily applied to the simplified prediction of the performance of filters in which the filter is divided into a series of equilibrium stages. By means of the porosity of the filter section the quantities of resin material and liquid phase are known. Consequently, the exchange equilibrium in each stage can be calculated. The effluent composition of the filter is given by the equilibrium in the last stage. By this means and by an appropriate assumption of the number of

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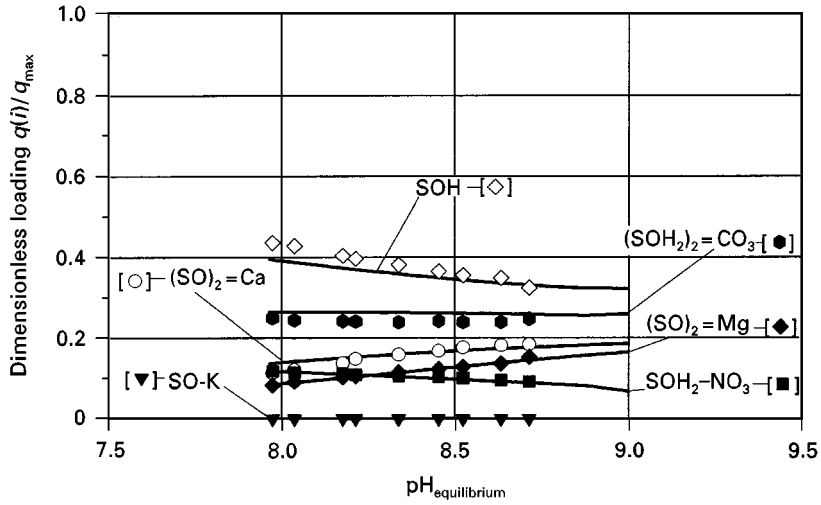

Figure 14 Comparison of experimental data and predicted loadings of activated carbon with inorganic species. Activated carbon: NORIT ROW 0.8 Supra.

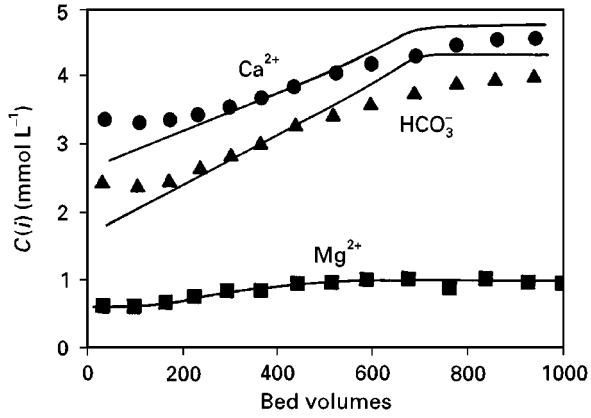

Figure 15 Comparison of experimental (●, ▲, ■) and predicted (—) breakthrough curves during softening/dealkalization of tap water. Resin: AMBERLITE IRC 50, regenerated by carbonic acid. Volume of resin, 1 L; throughput, 6.9 BV h^{-1}; feed: Ca^{2+} = 2.44 mmol L^{-1}; Mg^{2+} = 0.48 mmol L^{-1}; HCO_3^- = 4.42 mmol L^{-1}.

equilibrium stages a fairly good agreement between experimental and predicted concentration histories can be obtained. **Figure 15** shows the comparison between experimental data and predicted developments of concentrations for a system with a weakly acidic resin which is applied for softening/dealkalization of tap water. Clearly a very satisfactory agreement is obtained.

Further Reading

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Theory of Ion Exchange

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Proper theoretical tools are necessary at all stages in the development of ion exchange applications. Firstly, in the laboratory, when a new application is being developed, theory is helpful in the design of new materials and necessary for the interpretation and quantification of research results. Secondly, theory is needed in the design of industrial and laboratory processes. When the process is being operated, theory is again useful to keep the process under optimal control.

Ion exchangers are used in very diverse applications in the laboratory and in industry. Considering this, and the fact that a very wide range of different substances can act as ion exchangers, it is not surprising to see in the literature that various sets of nomenclature, conventions and diverse theories exist, reflecting the special features of the applications or materials involved. For instance, one finds rather different definitions for several basic terms of ion exchange in the field of water purification compared to those used in ion exchange chromatography and even diversity in the terminology can be seen within the field of ion chromatography. It is inevitable that various theories must exist for the functioning of different types of ion exchangers, but the